Advanced Surface Engineering Division
Room A215 - Session SE+PS-ThM

Plasma-assisted Surface Modification and Deposition Processes

Moderators: Robert Franz, Montanuniversität Leoben, Jianliang Lin, Southwest Research Institute

8:00am **SE+PS-ThM-1 Core/Shell Particles using a Plasma-based Reactors*, Santiago Vargas-Giraldo,* *D Galeano-Osorio, C Castano,* Virginia Commonwealth University

Nano-size and micro-size manufacturing have found an invaluable tool in plasma-assisted materials deposition techniques. Primarily, plasma-assisted physical vapor deposition (PAPVD) methods are clean, reliable and flexible to develop films and coatings. Materials produced by PAPVD may lead to stable structures and stoichiometries that are not possible on other processes. On the other hand, core/shell systems have dragged high attention due to their unique properties. These structures exhibit high surface area, and the interfacial interaction between the core and the shell leads to complex chemistries and transfer phenomena. This work presents an innovative approach to synthesize shells for existing particles using sputtering equipment. It demonstrates the challenges for the direct implementation of magnetron sputtering to obtain single and double shells on glass microspheres. First, a simple flat sample stage was used to discuss the prominent structural and conformability imperfections due to shadowing effects on 3D cores. To overcome this limitation, a new sample stage to manipulate the core particles under vacuum for more uniform shell formation was designed. As proof of concept, various metals and metal oxide shells over glass micro-size spheres were obtained. Extensive materials characterization of the newly formed structures was performed. The results are the groundwork for a myriad of technological applications.

8:20am **SE+PS-ThM-2 Formation Mechanisms of Converted Layer During Erosion of Composite Al-Cr Arc Cathodes*, Mehran Golizadeh*,** *F Mendez Martin, B Rashkova,* Montanuniversität Leoben, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Lechbruck am See, Germany*; R Franz,* Montanuniversität Leoben, Austria

Cathodic arc deposition (CAD) is a well-established physical vapor deposition technique which is characterized by a highly ionized plasma emitted from the cathode. The energy of the ions in the plasma ranges from 20 to some 100 eV, depending on the cathode material and the discharge conditions. These energetic and highly ionized plasmas significantly influence film growth mechanism and, e.g., high-temperature phases can be stabilized at typically low deposition temperatures in CAD. The plasma properties are influenced by the properties of the converted layer which forms on the surface of composite cathodes due to local consecutive melting-solidification cycles caused by the motion of the cathode spot over the cathode surface. Therefore, a detailed understanding of the formation mechanism and properties of the converted layer is essential to understand and manipulate plasma properties.

Within the current work, composite cathodes with composition of $Al_{0.5}Cr_{0.5}$ but different grain size, namely 80 and 1200 µm, were eroded in inert Ar gas at a pressure of 1 Pa applying a current of 60 A. A short erosion time of 30 s enabled us to capture single craters left behind by a cathode spot. A cross-section of the crater prepared using focused ion beam (FIB) showed the liquid pool formed by the cathode spot was violently deformed by plasma pressure, pushing the liquid out of the crater to the rim and surrounding space (macroparticles). The leftover liquid was rapidly quenched and there was almost no heat-affected zone below the crater. This finding shows that solid-state diffusion plays a negligible rule in the formation of the converted layer.

Further, cross-sections of the cathodes eroded for 1h were prepared by conventional metallography and FIB. Detailed microstructural and phase analysis using transmission electron microscopy and transmission Kikuchi diffraction together with cross-sectional study of single craters revealed that the converted layer is formed in a way that the rim of a crater fills the neighbouring craters due to step erosion. The splashes ejected from craters by plasma pressure also contribute to forming the converted layer. The later mechanism can be dominating depending on the topography of the cathode surface, which was confirmed by the erosion of the cathodes with 1200 µm grain size.

8:40am **SE+PS-ThM-3 Self-organization of Plasma in RF Magnetron Sputtering*, Matjaz Panjan,*** Jozef Stefan Institute, Slovenia

Self-organization of magnetron plasma in so-called spokes has been previously reported for pulsed [1, 2] and continuous magnetron discharges [3]. In this presentation, we will demonstrate that spokes also form in oscillatory RF magnetron sputtering regime [4]. We used an ICCD camera and electrical probes to investigate the rotating plasma patterns. The spokes in RFMS were compared to the spokes in classical DCMS at similar discharge conditions. In both regimes, stable plasma patterns were observed for a wide range of discharge parameters. For similar gas pressures and discharge powers, the number of spokes in the RFMS regime was always larger than in the DCMS regime. The number of spokes changed sequentially with the increasing working gas pressure for both magnetron operations. In the DCMS regime, a single spoke was observed at the lowest argon pressure (0.25 Pa) and a second spoke was observed only at the highest pressure (2 Pa). In the same pressure range, the plasma in the RFMS regime displayed four spokes at the lowest pressure and six or seven spokes at the highest pressure. The influence of discharge power on the number of spokes was less pronounced for both magnetron regimes. Spoke patterns were analyzed by examining the inelastic collisions between electrons and argon atoms. For this purpose, we simulated the dissipation of electron energy in the drift direction and compared the calculations to the length and number of spokes for particular discharge conditions. Overall, the simulations agree well with the observed plasma patterns in DCMS and RFMS.

[1] A. Anders *et al.*, *J. Appl. Phys.*, **111** (2012) 053304

[2] A. Ehiasarian *et al., Appl. Phys. Lett.*, **100** (2012) 11410

[3] M. Panjan *et al.*, *Plasma Sources Sci. Technol.*, **24** (2015) 065010

[4] M. Panjan accepted for publication in *J. Appl. Phys.* (2019)

9:00am **SE+PS-ThM-4 Study of High Power Pulsed Magnetron Sputtering Discharge with Positive Bias on the Target after the Main Pulse*, Ivan Shchelkanov,*** *T Houlahan, J McLain, I Haehnlein, B Jurczyk, R Stubbers,* Starfire Industries LLC*; D Barlaz, D Ruzic,* University of Illinois at Urbana-Champaign

Low-pressure magnetron sputtering is a well-established industry standard for high quality thin film deposition. Among different types of magnetron sputtering, High Power Pulsed Magnetron Sputtering (HPPMS), also called High Power Impulse Magnetron Sputtering (HIPIMS), offers the highest ion fraction of sputtered material, which dramatically increases the options available for thin film synthesis. The highly ionized sputtered material assists in multilayer film growth leading to more adhesive, dense, and smoother films as compared to conventional DC Magnetron Sputtering (dcMS) techniques, without the need for extra plasma-assisting elements and techniques in the process. Unfortunately, HPPMS typically suffers from low deposition rates as compared to dcMS[1]. Various attempts have been made to overcome this drawback, among them are: more efficient magnetic field configurations [2-6], HPPMS operation with extreme target conditions [7,8], or the application of a pulsed positive bias onto the sputtered target to control the plasma potential after the main HPPMS pulse [9]. Operation with a positive voltage KICK at the end of the main HPPMS pulse allows for the deposition of multilayer coatings onto a cold, grounded substrate with better adhesion than is typical of a simple HPPMS discharge. Furthermore, for grounded substrates positioned at glancing angles with respect to the sputtered magnetron cathode, the deposited coatings exhibit a very dense structure and great adhesion to the substrate even when deposited onto the inside wall of high aspect ratio vias. To fully understand limits, effects, and drawbacks of the positive KICK, its influence on plasma parameters, deposition rate, coatings structure, and adhesion are discussed.

[1] F.Papa, et al., 2011 Thin Solid Films 520.5 1559-1563.

[2] P. Raman, et al., Journal of Vacuum Science & Technology A 33.3 (2015): 031304.

[3] P. Raman, et al., Journal of Applied Physics, Volume 120, Issue 16, Page 163301 (2016)

[4] J. McLain, et al., Vacuum, Volume 155, Page 559-565 (2018)

[5] P. Raman, et al., Vacuum, Volume 156, Page 9-19 (2018)

[6] P. Raman, et al., Journal of Applied Physics, Volume 120, Issue 16, Page 163301 (2016)

[7] A.V.Tumarkin, et al., Surface and Coatings Technology. 2016. Vol. 293. P. 42–47

[8] A.V.Kaziev et al., Surface and Coatings Technology. 2016. Vol. 293. P. 48–54

[9] B. Wu et al., Vacuum, Volume 150, Page 216-221 (2018)

9:20am **SE+PS-ThM-5 Innovative PVD Strategies for the Design of Novel TiO_2-based Photoanode Utilized in Dye-sensitized Solar Cells*, Rony Snyders,*** University of Mons, Belgium **INVITED**

In view of the environmental challenges that our societies face, it is accepted that the development of alternative and renewable energy sources is a must. If solar energy is recognized as one of the most promising, it is still necessary to improve the solar cell technologies. Among others, Dye Sensitized Solar Cells (DSSC) are often seen as one of the ideal technological approach if several issues are fixed. One of the key problem associated with the implementation of these cells if related to the photoanode performances, specifically in terms of charge transport. Indeed, the standard photoanode based on TiO powder often exhibit a too high electrical resistivity associated with the intrinsic properties of the material.

During the past years, we have worked on the development of alternatives TiO_2-basedmaterial in order to solve the encountered problems. More precisely we have studied the growth of (N-doped) nano-sculpted TiO_2 films by using reactive magnetron sputtering in glancing angle deposition. Concerning the doping, co-reactive deposition as well as ion implantation have been evaluated. All samples have been thoroughly characterized by state-of-the-art techniques and, for most of them, tested in DSSCs.

The results demonstrate that our approach is versatile allowing to control the morphology of the TiO_2 films at the nanoscale, and therefore to tune the capability of the material to adsorb the active dye. Specifically, we showed that a combination of our films with conventional TiO_2 nanoparticles could be a promising approach. In addition, we also demonstrate that the phase constitution of the nano-sculpted films can be optimized in the form of a core-shell anatase/rutile structure in order to improve the charge transport. On the other hand, the study of the N doping reveals that it is possible to finely control the position of the N atom (substitutional vs intersticial) as a function of the experimental parameters. In this context, we demonstrated that the O vacancies density favor the substitutional doping. Finally, w e even showed that p type TiO_2:N films presenting good electrical and optical properties can be synthesized. This last result is of particular interest for the development of “full TiO_2” tandem DSSCs.

11:00am **SE+PS-ThM-10 Enhancing the Far Ultra-Violet Optical Properties of Aluminum Mirrors with a Single Step Approach to Oxide Removal and Fluorine Passivation*, David Boris,*** U.S. Naval Research Laboratory*; A Kozen, S Rosenberg,* American Society for Engineering Education (residing at U.S. Naval Research Laboratory)*; J del Hoyo, G Richardson, M Quijada,* NASA Goddard Spaceflight Center*; S Walton,* U.S. Naval Research Laboratory

Astronomical measurements in the Far Ultra-Violet (FUV, 90-200nm) require the use of aluminum thin films due to aluminum’s high reflectivity over this wavelength range. Unfortunately, the native aluminum oxide layer formed in atmosphere is strongly absorbing in this wavelength range, requiring that the aluminum films be passivated with a dielectric that inhibits oxidation. Due to the fast oxidation of aluminum, a simultaneous etch and deposition process is desirable to both eliminate the native aluminum oxide after growth and replace it with a different passivation coating layer. Optical measurements in the FUV range are some of the most challenging due to limited selection of low reflectivity coatings available for use on aluminum thin films. Typically magnesium fluoride (MgF_2) or lithium fluoride (LiF) coatings are used for these passivation purposes but each has its problems. MgF_2 has an absorption cutoff at 115 nm occluding a critical part of the FUV spectrum. LiF has a lower absorption cutoff at 102.5 nm, but is hygroscopic and thus susceptible to degradation in ambient conditions. A promising alternative to these coating materials is AlF_3, which theoretically can provide reflectivity greater than 50% down to 100 nm if the coating is sufficiently thin. In this work, we explore the use of electron beam generated plasmas to simultaneously etch the native oxide layer from aluminum thin films while depositing an AlF_3 capping layer to passivate the aluminum metal reflector. XPS measurements indicate that this approach is capable of producing very thin (<5 nm) AlF_3 films with some mild (<10%) oxygen contamination. We will discuss the impact of plasma power, plasma chemistry, and plasma exposure time on the composition and structure of the passivation layer and how those parameters effect the optical properties. This work is partially supported by the Office of Naval Research, the Naval Research Laboratory base program, and NASA Strategic Astrophysics Technology (SAT) grant No. NNH177ZDA001N

11:20am **SE+PS-ThM-11 Improving the Crystallinity of Inorganic Coatings Synthesized by Atmospheric Plasma using a New Device for Heating the Substrate*, Antoine Remy,*** *M Fall, F Reniers,* Université Libre de Bruxelles, Belgium

The deposition of good quality crystalline inorganic coatings by atmospheric pressure dielectric barrier discharge remains a challenge. Thanks to an original coupling of a substrate heating device based on an inductive current loop and located under the dielectric and an atmospheric pressure dielectric barrier discharge, we show that one can deposit in one step crystalline vanadium oxide and titanium oxide, with grain sizes bigger than those achieved by post-deposition annealing. As case study, vanadium oxide and titanium oxide are chosen. The respective precursors (vanadium oxytriisopropoxide - VOTP and titanium tetraisopropoxide – TTIP) are injected as vapors in a home made reactor with argon acting as carrier gas and main plasma gas. Oxygen is injected as reactant in the chamber. The DBD operates using a G10S-V AFS generator, at a frequency of 19 kHz, and with an injected power comprised between 0 and 80 W. The heating unit consists in a inductively coupled device located under the bottom electrode and dielectric and a susceptor place between the substrate and the dielectric. Thanks to a modified design of the bottom electrode, the induction loop does not heat said electrode, but the Eddy current heats only the susceptor, and the substrate. It is shown that this device allows the direct synthesis of crystalline orthorhombic V_2O_5 at 300°C, and of anatase TiO_2 at 400°C. A comparison with coatings deposited at room temperature and annealed at 300 and 400°C respectively shows that the coatings deposited on the heated substrate exhibit larger grain sizes. This original combination of an atmospheric pressure plasma DBD and a device to heat inductively the substrate shows that one can obtain good crystallinity for inorganic coatings, and opens potentially new opportunities for the deposition of such coatings by atmospheric plasma.

11:40am **SE+PS-ThM-12 Improved Nitride Formation on Titanium Substrates by Femtosecond Laser Processing with Secondary Plasma*, Jeremy Mettler,*** *D Barlaz,* University of Illinois at Urbana-Champaign*; B Jurczyk,* Starfire Industries LLC*; D Ruzic,* University of Illinois at Urbana-Champaign

We discuss the development of a plasma-enhanced, laser-induced surface conversion process for forming TiN, a common coating favored for its hardness and corrosion resistance. This process uses a pulsed femtosecond laser to provide localized energy deposition at the Ti surface, along with a secondary plasma to supply reactive N species. This method allows the surface conversion to be conducted in a single pass, rather than requiring a pretreatment step in Ar atmosphere for oxygen removal. The nitrogen radicals react preferentially where the laser provides sufficient energy to cause conversion of the native oxide layer. The conversion efficiency was investigated for DC and RF plasmas, as well as for different plasma powers, pressures, N precursors, and sample biases. Preliminary results with no secondary plasma achieved surface conversions of up to 9% TiN, measured using XPS. The inclusion of a secondary plasma provides a marked improvement over this previous result, both in terms of oxide removal and nitride formation. Laser powers for this work were between 3-5 W. A Langmuir probe diagnostic was used to compare plasma density at different powers (on the order of 100 W) and for different compositions.

12:00pm **SE+PS-ThM-13 Characterizing the Spatially Dependent Properties of Plasma Polymerized Acrylic Acid Films*, Karyn Jarvis,*** *S McArthur,* Swinburne University of Technology, Australia

Plasma polymer films have been deposited on planar surfaces for a wide variety of applications, such as controlling cell growth or adding linker molecules for biosensors. They can however also be deposited onto three dimensional objects, such as tissue engineering scaffolds, biomedical implants or 3D printed devices. Coating three dimensional objects however is more complex as greater monomer fragmentation occurs closer to the electrode. It is therefore important to understand the properties of the plasma polymer films that will be deposited when a sample is different distances from the electrode. The use of plasma polymer films in biomedical applications also requires suitably stable films under physiological conditions, which will also be influenced by the distance from the electrode. Significant changes in film properties in aqueous conditions have serious implications on the incorporation of these films in biomedical devices.

Acrylic acid is a commonly used monomer for plasma polymerization to produce negatively charged carboxylic acid terminated surfaces, which

have been used for a number of biomedical applications by manipulating cell growth. To gain a greater understanding of the spatially dependent behavior of plasma polymerized acrylic acid (ppAAc) films deposited in our custom-built stainless steel T-shaped reactor, ppAAc films were deposited at varying distances from the electrode (30 – 190 mm) at different deposition powers (5 – 80 W). The surface chemistry was analysed with X-ray photoelectron spectroscopy (XPS) while the film thickness was determined using spectroscopic ellipsometry. Aqueous stability was determined via immersion in Milli-Q. The film thicknesses decreased while the carboxyl group concentrations increased as the distance from the electrode increased and/or the deposition power decreased due to reduced monomer fragmentation further from the electrode and at lower powers. The aqueous stability of the films deposited further from the electrode increased as the deposition power increased. At 10 W, the film 30 mm from the electrode showed no decrease in film thickness after aqueous immersion while the films deposited 110 and 190 mm from the electrode were completely removed. Minimal film loss for the films deposited at 110 mm required a deposition power of 30 W while 60 W was required for minimal film loss for films deposited at 190 mm from the electrode. This work highlights the importance of having a spatially well characterized plasma reactor to enable the deposition of plasma polymer films with the desired properties, which has significant implications on the incorporation of these films into a number of applications.

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